



144055 Development of "n- and p-type Doped" Perovskite Single Crystals

Ho-Yong Lee
INDUSTRY-UNIVERSITY COOPERATION FOUNDATION.SUNMOON UNIV.

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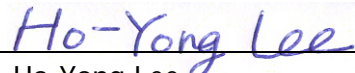
Final Report for AOARD Grant FA2386-14-1-4055

**"Development of "*n*- and *p*-type Doped" Perovskite Single Crystals
Using Solid-State Single Crystal Growth (SSCG) Technique"**

Principal Investigator:	Prof. Ho-Yong Lee Sunmoon University Department of Advanced Materials Engineering 70, Sunmoon-Ro 221, Tangjeong-Myeon, Asan-si, Chungnam, 336-708 (Postal Code), KOREA Tel) 82-41-530-2366 (Office); 82-10-3301-2366 (Mobile) Fax) 82-41-584-2367 E-mail) hlee.ceracomp@gmail.com ; hlee@sunmoon.ac.kr
Administrative Point of Contact:	Goang-Hyon Ryu Sunmoon University Industry-University Cooperation Foundation Tel) 82-41-530-2641 (Office) E-mail) ryu01@sunmoon.ac.kr
Submitted to:	Dr. Ken Caster International Program Office Asian Office of Aerospace Research & Development (AOARD) Tokyo, Japan E-mail) kenneth.caster@us.af.mil ; kcchem83.japan@gmail.com

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Ho-Yong Lee

September 01, 2017
Date

Abstract:

In this project the solid-state growth of "n- and p-type doped" perovskite single crystals [(1) paraelectric SrTiO_3 , (2) normal ferroelectric BaTiO_3 , (3) relaxor ferroelectric $0.85\text{BaTiO}_3\text{-}0.15\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$, and (4) antiferroelectric PbZrO_3] have been tried. **Among them "n- and p-type doped" BaTiO_3 single crystals have been successfully fabricated.** And their bi-crystals containing a twin or twist boundary are also fabricated using diffusion bonding process of two single crystal plates. These results demonstrate that the SSCG (solid-state single crystal growth) technique are suitable to grow a variety of "n- and p-type doped" perovskite single crystals of complicated compositions.

The Fe-doped (001) BaTiO_3 single crystals show an ultrahigh strain of 0.8% at 1 kV/mm ($S_{\text{max}}/E_{\text{max}} = 15,000 \text{ pm/V}$) which is 30 times higher than PZT ceramics and 7.5 times higher than PMN-PT single crystals. Therefore the BaTiO_3 single crystals having "ultrahigh" unipolar strains will be used for actuator, sensor, and transducer applications.

The research is anticipated to guide the practical development of functional perovskite single crystals of critical importance to the Air Force mission. The fundamental information gained will be presented and integrated into scientific workshops and symposia to catalyze expansion of the fundamental work and to also inspire practical solutions to developing improved non-linear dielectric materials for extreme environments.

1. Introduction

There are several classes of materials that can be used to develop new non-linear dielectrics for high-voltage and high-power applications. A major need is to better understand their individual limitations at high electric field strengths in terms of the high-field conductivity and electrical breakdown. The phenomena that lead to failure are complex and need more extensive scientific understanding, particularly in regard to polarization and conduction at interfaces, the specific charge transfer process, and point defect (and thus field) distributions in the vicinity of microstructural features and electrodes, how these are coupled, and how they evolve with time under electrical bias. Despite substantial work in non-linear dielectrics, such knowledge remains unknown and limits current strategies for improving high-temperature and high-field performance dielectrics.

In order to provide a fundamental, mechanistic understanding of interface-mediated polarization, conduction, degradation, and breakdown processes in non-linear dielectric materials, the majority of experiments utilize “n- and p-type doped” perovskite single crystals such as (1) paraelectric SrTiO_3 , (2) normal ferroelectric BaTiO_3 , (3) weakly coupled relaxor $0.85\text{BaTiO}_3\text{-}0.15\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [BT-15BMT], and (4) antiferroelectric PbZrO_3 [PZ]. Bi-crystals of SrTiO_3 and BaTiO_3 will be used to conduct prototype experiments on artificial grain boundaries. However, it has been well known that it is very difficult or impossible to grow the single crystals. Therefore their bi-crystals cannot be easily made because of difficulty in growing the single crystals. So we need to use and develop a new single crystal growth method which is suitable to grow chemically uniform and large “n- and p-type doped” perovskite single crystals.

Figure 1 shows the methods of single crystal growth. The conventional crystal growth techniques for perovskite single crystals including flux technique or Bridgman method have critical limitations; high production cost and compositional inhomogeneity throughout the crystal. These limitations result from a complicated melting step of major constituents during crystal growth. Especially, it is very difficult to grow chemically uniform single crystals of $0.85\text{BaTiO}_3\text{-}0.15\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BT-15BMT) and PbZrO_3 (PZ), because of its high solid solubility (BT-15BMT) and incongruent melting behavior (PZ), by using the conventional crystal growth methods such flux and Bridgman methods. Therefore the successful growth of large and chemically uniform BT-15BMT and PZ single crystals has not been reported yet.

In this project, we will develop a more convenient and cost-effective fabrication process for growing perovskite single crystals with no melting step of major components. The perovskite single crystals will be directly grown from polycrystalline precursors by the SSCG method, as shown in Fig. 2. Since the growth of perovskite single crystals will proceed at a constant

temperature without a melting step, the grown crystals are chemically homogeneous and the production cost becomes much lower.

Figure 3 shows the previous investigation of solid-state growth of BaTiO₃ single crystals. A small BaTiO₃ single crystal (as a seed) was diffusion bonded to a polycrystalline BaTiO₃ ceramics and heat-treated at an appropriate temperature for growth of the seed crystal. During the heat-treatment, however, the seed single crystal grew up to a few millimeters. The single crystal growth was very limited and the growth rate was very low. So in the previous investigation it was not possible to grow large BaTiO₃ single crystals by using the solid-state method because the abnormal grain growth was not controlled successfully.

During the heat-treatment of a polycrystalline material, a few grains sometimes grow extensively at the expense of fine matrix grains a process usually referred to as abnormal grain growth (AGG). Because of the appearance of large abnormal grains, the grain size distribution changes from uni-modal distribution of grain size to bimodal distribution of grain size, as shown in Fig. 4. During normal grain growth (NGG), however, the grain size distribution of a polycrystalline body does not change, as shown in Fig. 4. The rate of AGG is orders of magnitude higher than that of normal grain growth. Therefore, when the number of abnormal grains is strictly controlled, the single crystal can be grown with a relatively high rate in the solid state. For growing a single crystal by AGG, the number of "nuclei" for AGG should be minimal. For this purpose, the seeds for AGG may also be provided externally. This process is called the solid-state single crystal growth (SSCG) method, and its principle is rather simple: let an external single crystal seed grow by consuming the fine matrix grains without melting the major constituents, as shown in Fig. 2. Since this process is not only quite cost-effective but also good for mass production of large single crystals, many researchers tried to grow single crystals by the SSCG method. The possibility of growing a single crystal by the SSCG was already demonstrated by NGK (ferrite) in Japan and GE (Al₂O₃) in USA.

Ceracomp has demonstrated that the number density of abnormal grains in sintered BaTiO₃ ceramics can be controlled, as shown in Fig. 5. By controlling the number density of abnormal grains in sintered BaTiO₃ ceramics, a large single crystal can be grown in a polycrystalline ceramics.

Figure 6 shows the SSCG process of BaTiO₃ that has been successfully established by Ceracomp. A small (001) BaTiO₃ single crystal seed was placed on the top of a sintered ceramics and heat-treated. During the heat-treatment, the seed crystal grew in to the ceramics and became a large single crystal. It occurred without melting of BaTiO₃ because the heat-treatment temperature was much lower than the melting temperature of BaTiO₃.

By using the SSCG process, a transparent BaTiO₃ single crystal could be grown as shown in Fig. 7. A “unique” BaTiO₃ single crystal with the compositional gradient (A Mn-, Cr-, and Ce-doped BaTiO₃ single crystal) could be also fabricated by using a BaTiO₃ ceramics with the same compositional gradient (Fig. 8). This result has demonstrated that the SSCG method is very suitable to fabrication of doped perovskite single crystals and makes it possible to grow compositionally uniform “n- and p-type doped” perovskite single crystals [(1) paraelectric SrTiO₃, (2) normal ferroelectric BaTiO₃, (3) relaxor ferroelectric 0.85BaTiO₃-0.15Bi(Mg_{0.5}Ti_{0.5})O₃ [BT-15BMT], and (4) antiferroelectric PbZrO₃ [PZ]].

Pb(Zr,Ti)O₃ [PZT] ceramics have been the main stay for high performance piezoelectric applications. Compositionally PZT ceramics lie near the MPB between the tetragonal and rhombohedral phases and MPB compositions exhibit anomalously high dielectric and piezoelectric properties. Many attempts to grow single crystals of PZT and PZ have been made by numerous researchers, resulting in crystallites too small to allow adequate property measurements, as shown in Fig. 9. In contrast to relaxor-PT crystal growth, PZT and PZ cannot be readily grown in single crystal form because of incongruent melting behavior of PZ as well as evaporation of volatile PbO during melting process. During incongruent melting of PZ, PZ decomposes to liquid and solid phase ZrO₂. The solid phase ZrO₂ in the liquid phase prevents continuous growth of PZ single crystals. In order to grow large PZ or PZT single crystals, therefore, a melting step of PZ should be avoided in the crystal growth process.

For the Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ [PMN-PT] system containing volatile PbO, a BaTiO₃ single crystal obtained by the SSCG method (Fig. 6) was used as a seed crystal. When a BaTiO₃ single crystal was placed on the top of a PMN-PT ceramics and then heat-treated, a PMN-PT single crystal grew hetero-epitaxially at the surface of the BaTiO₃ single crystal. Figure 10 shows an experimental procedure for growing chemically homogeneous and fully dense PMN-PT single crystal. Hot pressing was very effective in densification of PMN-PT ceramics. When a seed crystal was grown in a hot-pressed ceramics, a fully dense PMN-PT single crystal was obtained as shown in Fig. 10.

Figure 11 shows the solid-state growth of Pb(Mg_{1/3}Nb_{2/3})O₃-Pb(Zr,Ti)O₃ [PMN-PZT] single crystals doped (a) Fe, (b) In, and (c) Mn. The PMN-PZT system includes a PZ component and thus shows incongruent melting behavior. Because of the incongruent melting of PZ as well as volatile PbO, the growth of large PMN-PZT single crystals has not been reported yet by using other crystal growth methods except the SSCG technique. Especially up to this time “n- or p-type doped” PMN-PZT single crystals could be grown only by the SSCG method.

The application of conventional melt growth techniques to “n- and p-type doped” perovskite single crystals [(1) paraelectric SrTiO₃, (2) normal ferroelectric BaTiO₃, (3) relaxor ferroelectric 0.85BaTiO₃-0.15Bi(Mg_{0.5}Ti_{0.5})O₃ [BT-15BMT], and (4) antiferroelectric PbZrO₃ [PZ]], such as flux,

Czochralski, zone melting, and Bridgman techniques, are limited by the several reasons shown in Fig. 12. The main reasons are (1) the destructive phase transition, (2) high PbO vapor pressure at the growth temperature, (3) incongruent melting behavior of PZ, and (4) phase stability, and (5) high solid solubility. These make the growth of “n- and p-type doped” perovskite single crystals complicated. Therefore the solid-state single crystal growth method could be the best way of growing compositionally uniform “n- and p-type doped” perovskite single crystals [(1) paraelectric SrTiO_3 , (2) normal ferroelectric BaTiO_3 , (3) relaxor ferroelectric $0.85\text{BaTiO}_3\text{-}0.15\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [BT-15BMT], and (4) antiferroelectric PbZrO_3 [PZ]].

The bi-crystals of “n- and p-type doped” perovskite single crystals can be made by a simple diffusion bonding process, as shown in Fig. 13. Fig. 13 shows the vertical cross sections, thermally etched at 1550°C for 1 h, of the *m* plane of an Al_2O_3 single crystal diffusion-bonded to (A) the *C* plane of an Al_2O_3 single crystal located at the top [**Bi-crystal**] and (B) the sintered Al_2O_3 polycrystal located at the bottom. And Fig. 14 shows the microstructures of cross sections of diffusion couples (Fig. 13) after heat-treatment in the presence of Fe_2O_3 at 1550°C ((A) *C-m* **bi-crystal** and (B) *m-P*). As shown in Figs. 13 and 14, the diffusion bonding process is very simple and effective to make bi-crystals containing a tilt or twist boundary.

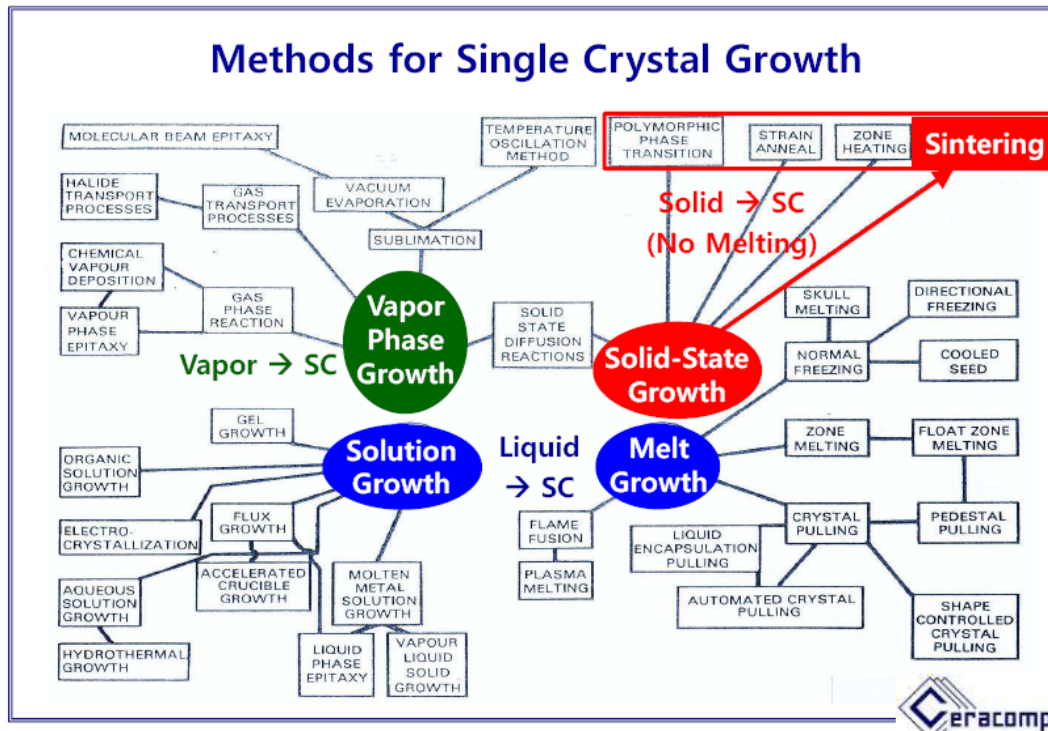


Fig. 1. Methods for single crystal growth
(Solid-state conversion from a polycrystalline ceramics to a single crystal).

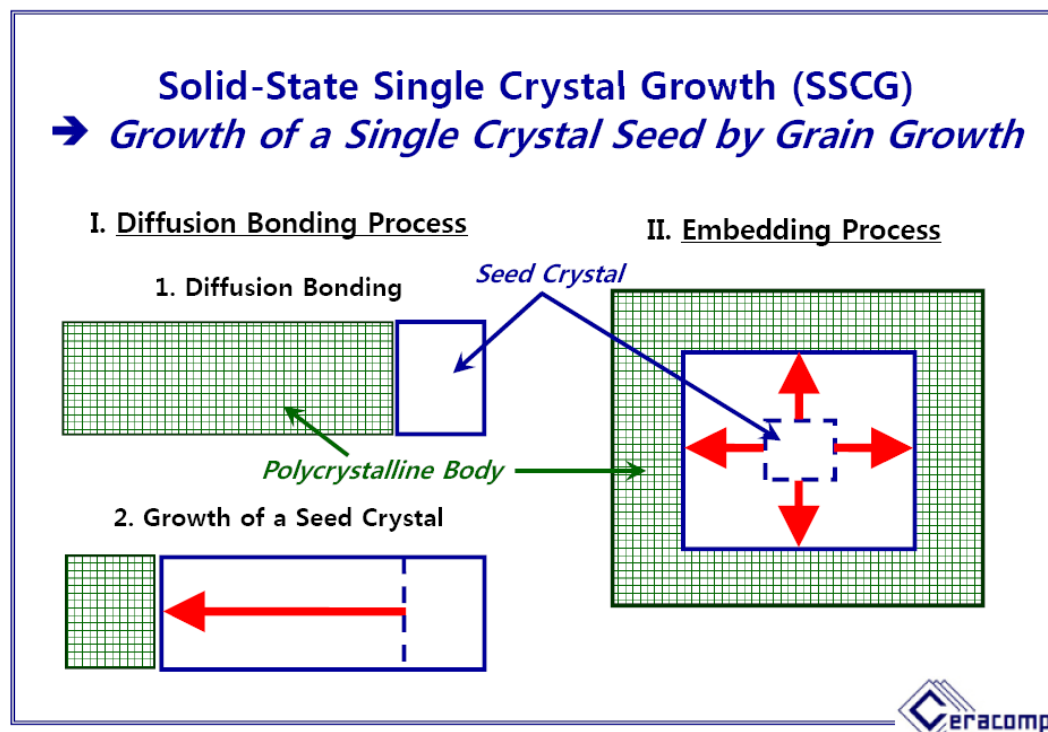
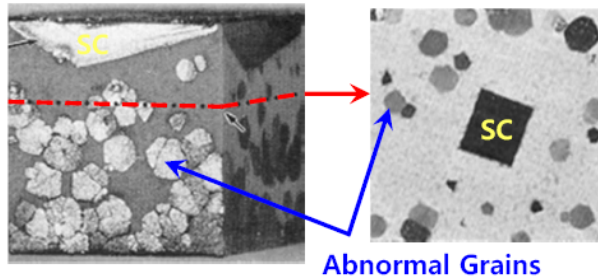
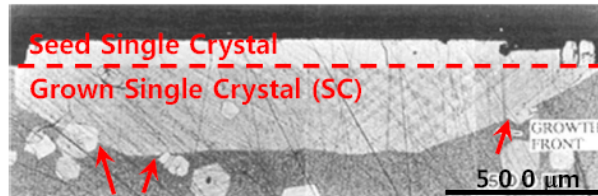


Fig. 2. Schematic of the solid-state single crystal growth (SSCG) method.

Fabrication of BaTiO₃ Single Crystals by Solid-State Grain Growth Method



Limitations

1. Slow Growth
2. Quality (Pores) of Single Crystals
3. **Small Single Crystal** (A few millimeters in size)

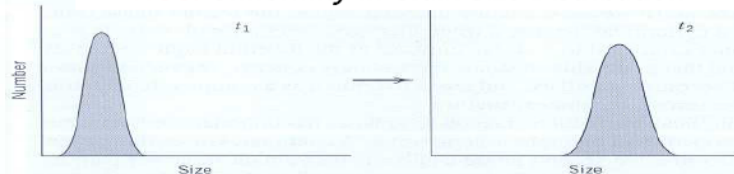
T. Yamamoto and T. Sakuma, J. Am. Ceram. Soc., 1994 (77)



Fig. 3. Solid-state growth of a BaTiO₃ single crystal in the previous study. In the previous study the abnormal grain growth was not successfully controlled.

Normal Grain Growth vs. Abnormal Grain Growth (NGG) (AGG)

NGG: Uniformity in Grain Size Distribution



AGG: Bimodal Distribution of Grain Size

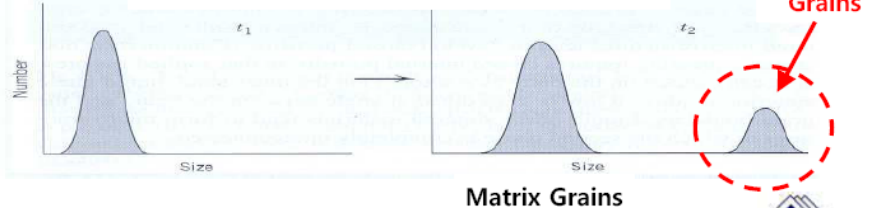


Fig. 4. Normal grain growth (NGG) vs. Abnormal grain growth (AGG).

Control of Number Density of Abnormal Grains in Sintered BaTiO_3

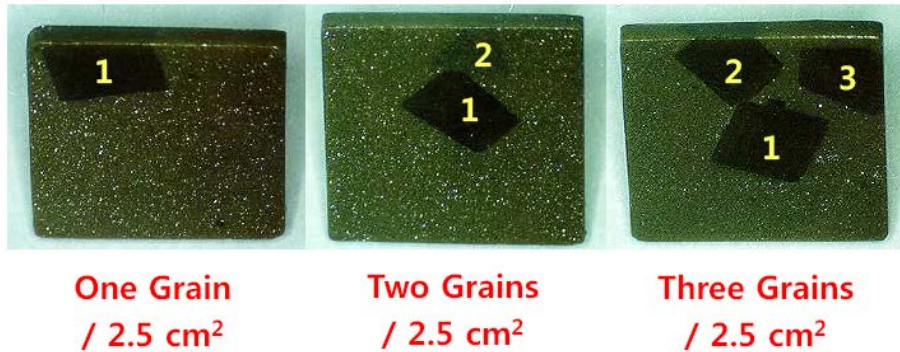


Fig. 5. Control of number density of abnormal grains in sintered BaTiO_3 ceramics.

"Solid-State Single Crystal Growth (SSCG)" Method

→ Growth of a Single Crystal in a Polycrystalline Body by Grain Growth



SSCG of $\text{Ba}(\text{Ti,Zr})\text{O}_3$:
Growth of a (100) Seed



Fig. 6. SSCG of a BaTiO_3 single crystal in a polycrystalline precursor.
by Ceracomp

**Transparent "High Density" BaTiO₃ Single Crystal
Grown by SSCG Method**

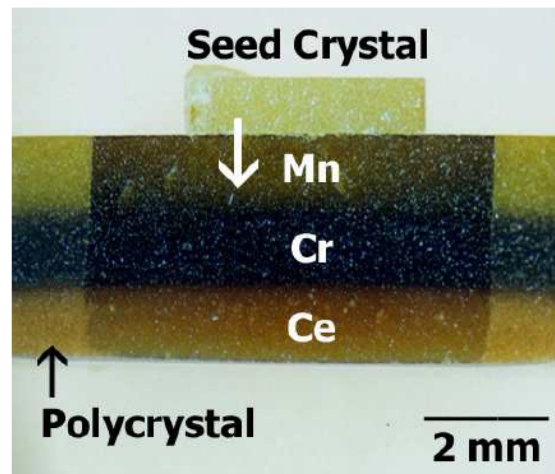


(001) Plate; [15x5x1 mm³]



Fig. 7. Growth of a transparent BaTiO₃ single crystal by SSCG technique.

**Growth of a BaTiO₃ Single Crystal
into Mn-, Cr-, and Ce-doped BaTiO₃ Ceramics**



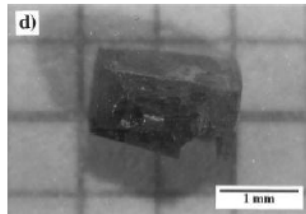
**"Rainbow"
BaTiO₃
Single
Crystal**



Fig. 8. Cross-section of a BaTiO₃ single crystal with the compositional gradient.
(A Mn-, Cr-, and Ce-doped BaTiO₃ single crystal)

Single Crystal Growth of PZT and Relaxor-PZT (MPB I)

1. **Incongruent melting of PZT** [$\text{Pb}(\text{Zr,Ti})\text{O}_3$] ($\text{PZT} \rightarrow \text{Liquid} + \text{ZrO}_2(\text{solid phase})$)
 \rightarrow It makes single crystal growth of PZT very difficult or impossible.
2. Flux or Bridgman method (Conventional crystal growth methods)
 \rightarrow not successful (only millimeter-sized single crystals)
3. Hydrothermal synthesis \rightarrow not successful (only millimeter-sized crystals)



Tetragonal PZT
 K. Yanagisawa et al.
 Journal of European Ceramic Society
 19, 1033~1036 (1999)

4. Solid-state crystal growth [SSCG] method \rightarrow Large PZT single crystals possible?
 (Because no melting of PZT is involved in the SSCG process.)



Fig. 9. Previous studies of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ [PZT] single crystal growth.

Growth of PMN-PT Single Crystals (> 1.5 inches) by SSCG

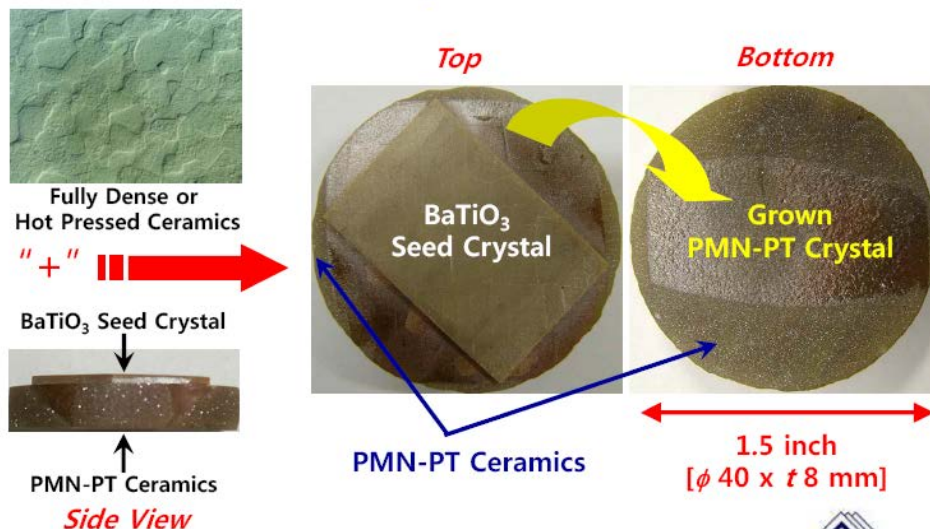


Fig. 10. Experimental procedure for SSCG of a PMN-PT single crystal.

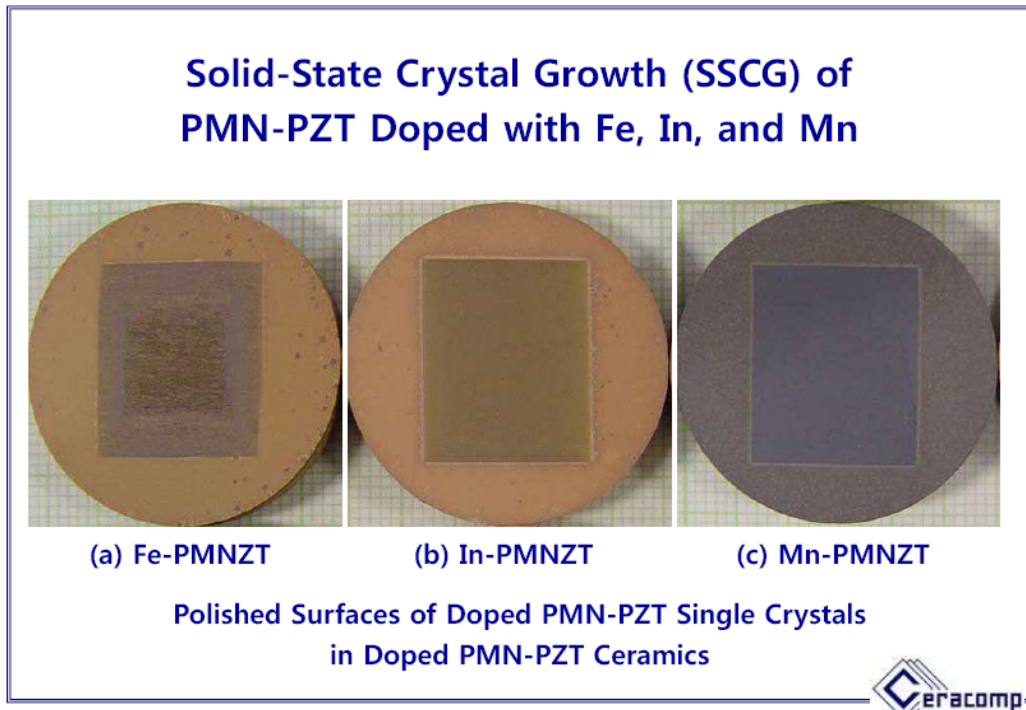


Fig. 11. Solid-state growth of PMN-PZT single crystals doped (a) Fe, (b) In, and (c) Mn.

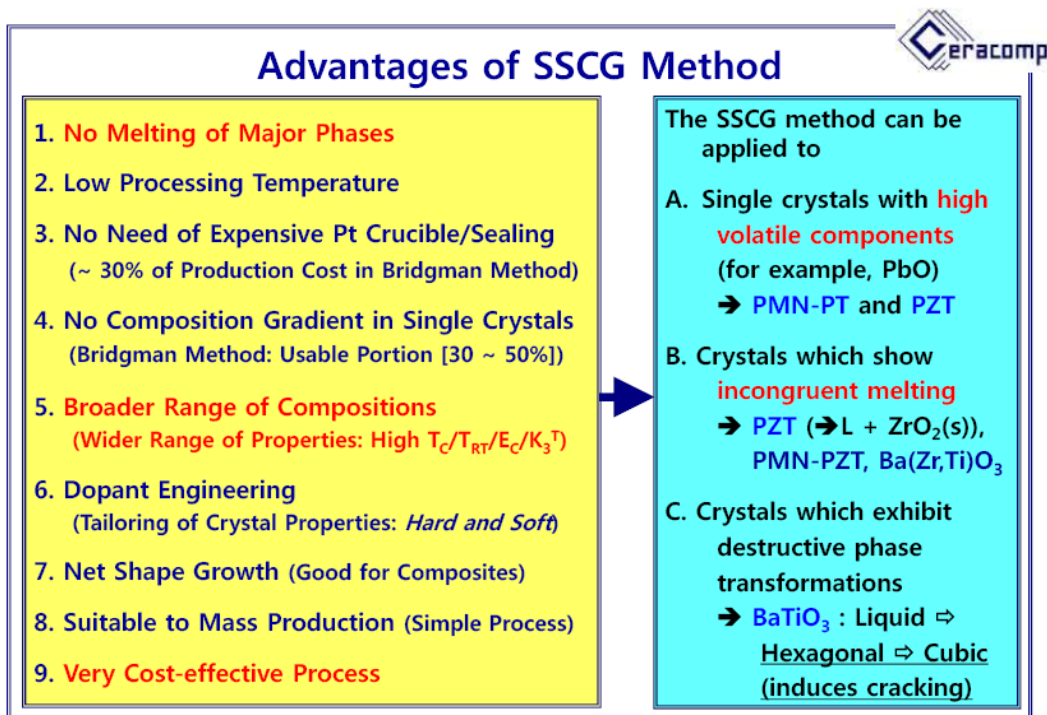


Fig. 12. Advantages of the SSCG method.

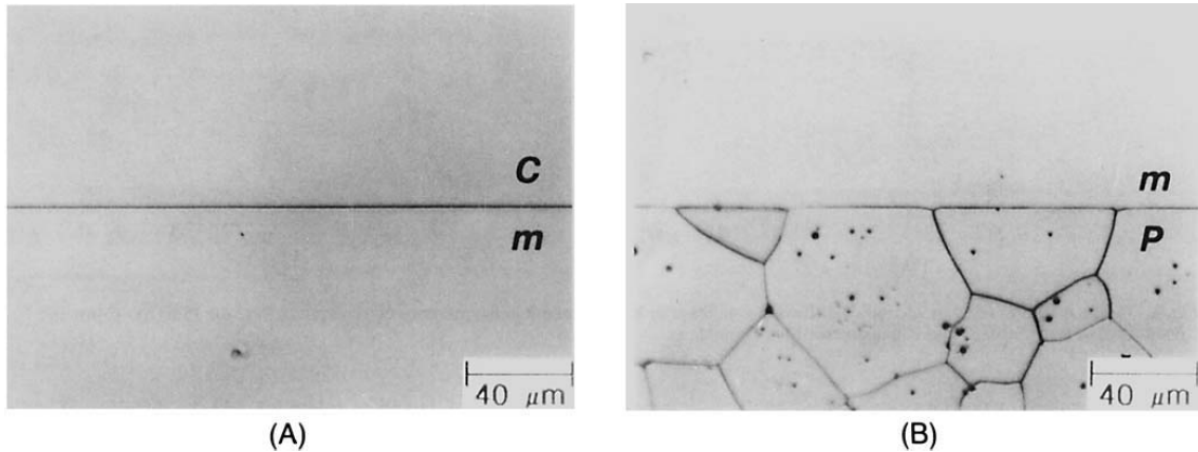


Fig. 13. Vertical cross sections, thermally etched at 1550°C for 1 h, of the *m* plane of an Al_2O_3 single crystal diffusion-bonded to (A) the *C* plane of an Al_2O_3 single crystal located at the top [Bi-crystal] and (B) the sintered Al_2O_3 polycrystal located at the bottom.

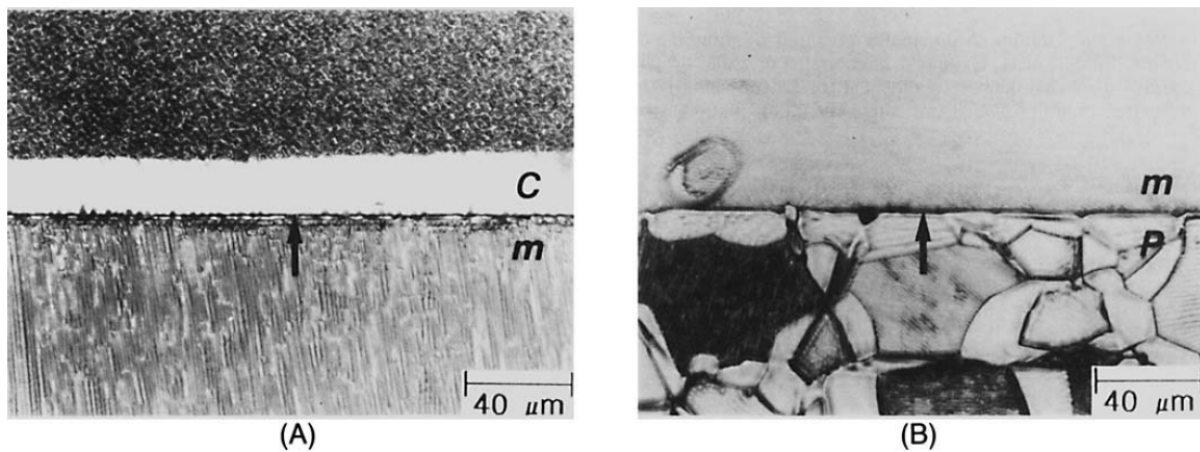


Fig. 14. Microstructures of cross sections of diffusion couples (Fig. 13) after heat-treatment in the presence of Fe_2O_3 at 1550°C ((A) *C-m* bi-crystal and (B) *m-P*). The arrow in each figure indicates the initial boundary.

3. Experimental Results and Discussion

In this project several different kinds of “n- and p-type doped” perovskite single crystals [(1) paraelectric SrTiO_3 , (2) normal ferroelectric BaTiO_3 , (3) relaxor ferroelectric $0.85\text{BaTiO}_3\text{-}0.15\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$, and (4) antiferroelectric PbZrO_3] have been tried to grow by using solid-state single crystal growth (SSCG) technique. And their bi-crystals containing a twin or twist boundary are also fabricated using diffusion bonding process of two single crystal plates. The focus of this effort will also include the characterization of both “n- and p-type doped” perovskite single crystals and their bi-crystals.

3-1. BaTiO_3 single crystals

3-1-1. Experimental Process

“n- and p-type doped” BaTiO_3 single crystals used in the present study were prepared by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of BaCO_3 , TiO_2 and several dopants (Ca, Ce, Co, Cr, Fe, La, Mg, Mn, Nb, and Nd), “n- and p-type doped” polycrystalline BaTiO_3 ceramics were obtained through a general sintering process. After weighing each raw material powder for “n- and p-type doped” BaTiO_3 compositions, they were mixed for 24 hours using ball-milling process, and calcined at $1,000^\circ\text{C}$ following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a BaTiO_3 seed single crystal was placed on the sintered body of “n- and p-type doped” BaTiO_3 , and the second heat treatment for solid-state single-crystal growth was carried out for 200 hours at different temperatures.

The BaTiO_3 seed single crystal was continuously grown into the “n- and p-type doped” polycrystalline BaTiO_3 body during the heat treatment process for single-crystal growth, and “n- and p-type doped” BaTiO_3 single crystals of a size larger than $25\times 25\times 5\text{ mm}^3$ were prepared as a result. Since no melting in BaTiO_3 occurred during single-crystal manufacturing process in the single-crystal growth method, composition gradients were not observed within the grown manufactured single crystal, giving rise to a chemical homogeneity. Thus-prepared single crystals larger than $25\times 25\times 5\text{ mm}^3$ in size were cut into a plate shape(specimen of $[3\times 3\times 0.5(\text{t})\text{ m}^3]$ for thickness mode measurement) and a square-column shape(specimen of $[1\times 1\times 5(\text{t})\text{ m}^3]$ for 33 mode measurement) single-crystal specimens, and an Au electrode was formed on the cut single-crystal plate by using vacuum deposition method. Dielectric and piezoelectric properties of the manufactured “n- and p-type doped” BaTiO_3 single crystals and polycrystalline ceramics were measured in accordance with the IEEE standard.

3-1-2. Experimental Results

All "*n*- and *p*-type doped" BaTiO₃ single crystals fabricated grown in this program are listed in Fig. 15. As shown in Fig. 15, **undoped, isovalent ion-doped (Ca, Ce, and Zr), *n*-type doped (La, Nb, Nd), and *p*-type doped (Cr, Co, Fe, Mg, and Mn) BaTiO₃ single crystals** are successfully grown by the SSCG technique.

Figure 16 shows the solid-state growth of "Cr"-doped BaTiO₃ single crystals. The (001) and (111) single crystals of "Cr"-doped BaTiO₃ are successfully grown from (001) and (111) seed crystals, respectively.

Figure 17 shows "5x5x1(t) mm₃" plates of "Fe"- and "Nb"-doped BaTiO₃ single crystals grown by the SSCG technique. And "5x5x1(t) mm₃" plates of "Mn"-, "Mg"-, and "Co"-doped BaTiO₃ single crystals are also shown in Fig. 18.

The density of BaTiO₃ single crystals can be increased by increasing the density of polycrystalline ceramics before SSCG process. The HP (hot press) process is very effective in increasing densities or decreasing porosities of polycrystalline ceramics. So in this study the HP process was used to increasing densities of polycrystalline ceramics as well as SSCG single crystals. Figure 19 shows the schematics of controlling the density and porosity of BaTiO₃ single crystals by using HP process. The "high density" BaTiO₃ single crystal fabricated by using HP (Hot Press) process is shown in Fig. 20. Because the BaTiO₃ single crystal is fully densified, it is transparent as shown in Fig. 20.

Figure 21 shows the polarization behaviors of (a) undoped, (b) Fe (Acceptor)-doped and (c) Nb (Donor)-doped (001) BaTiO₃ single crystals. Compared to undoped BaTiO₃ single crystals, Fe (Acceptor)-doped BaTiO₃ single crystals show the higher polarization. However, Nb (Donor)-doped BaTiO₃ single crystals show the lower polarization.

Figure 22 shows the bipolar strains of (a) undoped, (b) Fe (Acceptor)-doped and (c) Nb (Donor)-doped (001) BaTiO₃ single crystals. Compared to undoped BaTiO₃ single crystals, Fe (Acceptor)-doped BaTiO₃ single crystals show the higher bipolar strain. However, Nb (Donor)-doped BaTiO₃ single crystals show the lower bipolar strain.

Figure 23 shows the unipolar strains of (a) undoped, (b) Fe (Acceptor)-doped and (c) Nb (Donor)-doped (001) BaTiO₃ single crystals. Compared to undoped BaTiO₃ single crystals, Fe (Acceptor)-doped BaTiO₃ single crystals show the higher unipolar strain. However, Nb (Donor)-doped BaTiO₃ single crystals show the lower unipolar strain.

In order to compare unipolar strains of (001) BaTiO₃ single crystals undoped, acceptor-doped and donor-doped, doped BaTiO₃ single crystals are prepared and their unipolar strains are measured, as shown in Fig. 24. Among all doped BaTiO₃ single crystals, Fe (Acceptor)-doped BaTiO₃ single crystals show the largest unipolar strain of 0.8% at 1 kV/mm. However, Nb (Donor)-doped BaTiO₃ single crystals show the lower unipolar strain.

Figure 25 shows the ultrahigh unipolar strains of (001) BaTiO₃ single crystals doped with Fe. **The unipolar strain was about of 0.8% at 1 kV/mm and thus its S_{\max}/E_{\max} was calculated to be about 15,000 pm/V.** When the unipolar strains of PZT ceramics ($d \sim 500$ pC/N), PMN-PT single crystals ($d_{33} \sim 2,000$ pC/N), and Fe-doped BaTiO₃ single crystals ($S_{\max}/E_{\max} = 15,000$ pm/V) are compared as shown in Fig. 26, the Fe-doped BaTiO₃ single crystals show the highest unipolar strain of 0.8% at 1 kV/mm which is 30 times higher than PZT ceramics and 7.5 times higher than PMN-PT single crystals. **This result demonstrates that Fe-doped BaTiO₃ single crystals ($S_{\max}/E_{\max} = 15,000$ pm/V) can be used for actuator application.**

Figure 27 shows 1-3 single crystal-epoxy composites and "flexible" SFC composites of Fe-doped BaTiO₃ single crystals. The BaTiO₃ single crystals having "ultrahigh" unipolar strains will be used for actuator, sensor, and transducer applications.

“*n*-” and “*p*-type” Doped BaTiO₃ Single Crystals Fabricated in this Program

1. The First Year (June 4, 2014 ~ June 3, 2015)

- 1-1. “Acceptor [*p*-type (Ionic)]”-doped BaTiO₃ SC → Fe, Mn
- 1-2. “Donor [*n*-type]”-doped BaTiO₃ SC → La, Nb

2. The Second Year (June 4, 2015 ~ June 3, 2016)

- 2-1. “Acceptor [*p*-type (Ionic)]”-doped BaTiO₃ SC → Fe, Mn, Cr, Co
- 2-2. “Donor [*n*-type]”-doped BaTiO₃ SC → La, Nb, Nd

3. The Second Year (June 4, 2016 ~ June 3, 2017)

- 2-1. “Acceptor [*p*-type (Ionic)]”-doped BaTiO₃ SC → Cr, Co, Mg
- 2-2. “Donor [*n*-type]”-doped BaTiO₃ SC → Nd
- 2-3. “Isvalent Ion [*neutral*]”-doped BaTiO₃ SC → Ca, Ce, Zr



Fig. 15. “*n*- and *p*-type doped” BaTiO₃ single crystals grown in this program

“Cr”-doped BaTiO₃ Single Crystals Grown by SSCG



Growth from (001) Seed

Growth from (111) Seed



Fig. 16. “Cr”-doped BaTiO₃ single crystals grown by using (001) and (111) seed crystals

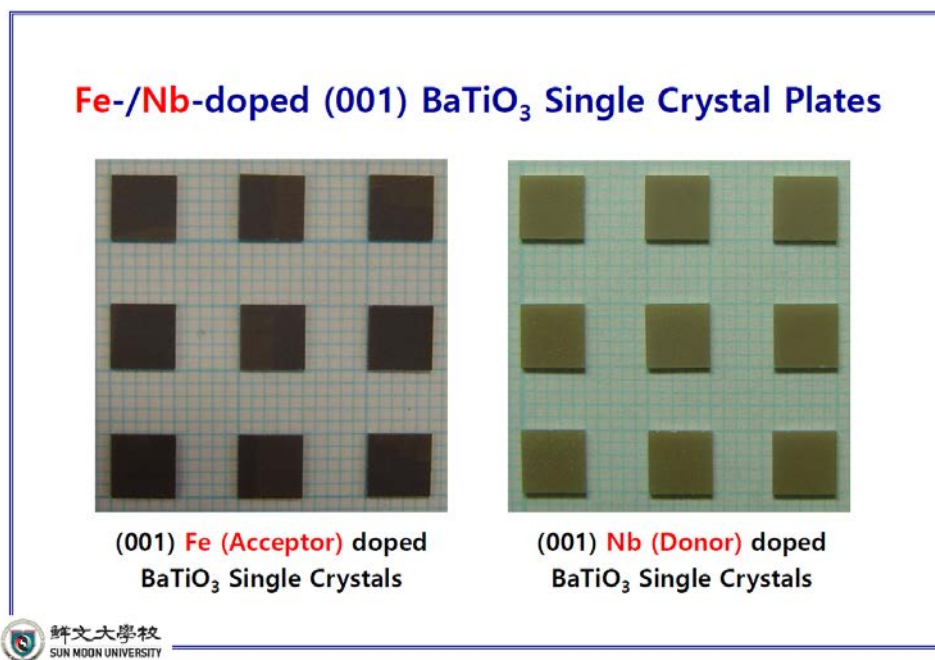


Fig. 17. "Fe"- and "Nb"-doped BaTiO₃ single crystals grown by SSCG technique

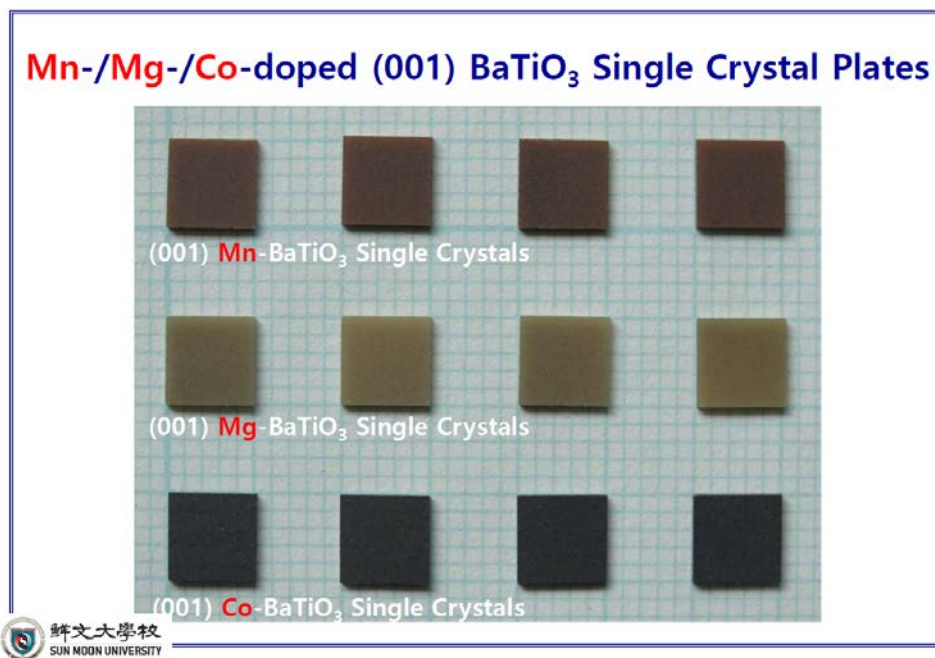


Fig. 18. "Mn"-, "Mg"-, and "Co"-doped BaTiO₃ single crystals grown by SSCG technique

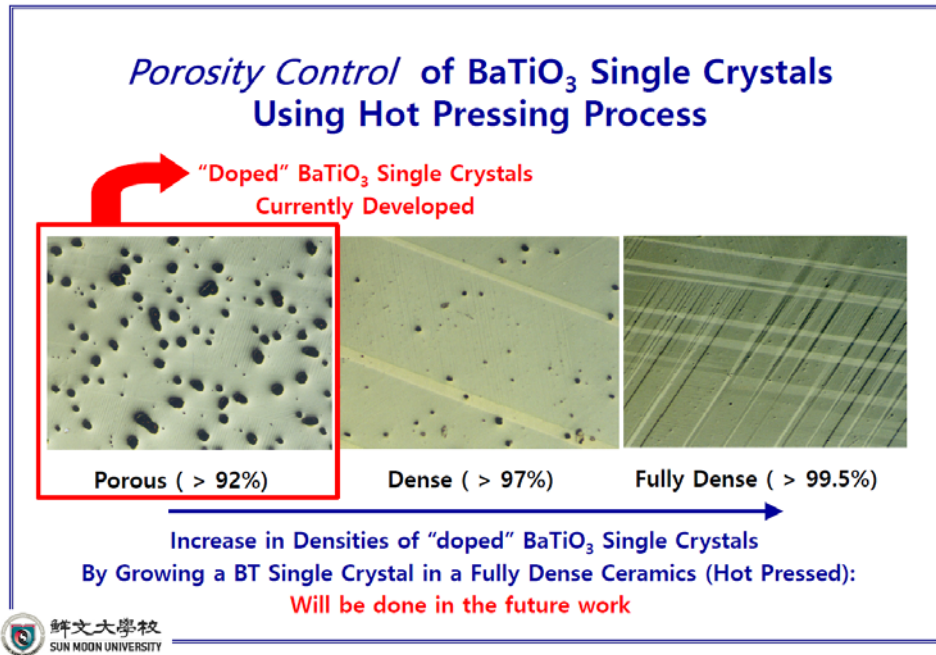


Fig. 19. Porosity Control of BaTiO₃ single crystals by using HP (Hot Press) process

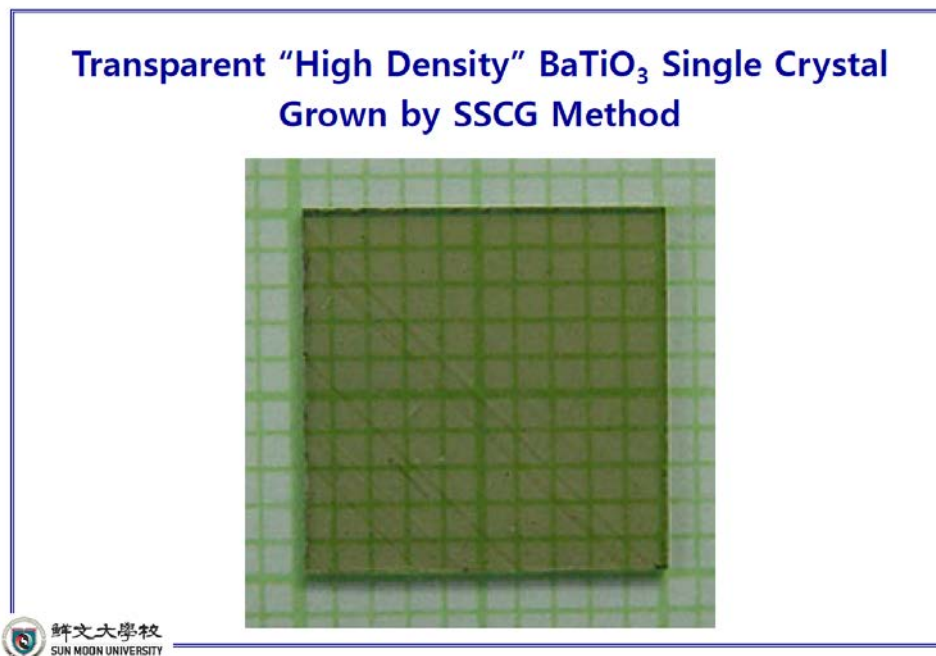


Fig. 20. Transparent “high density” BaTiO₃ single crystals
Fabricated by using HP (Hot Press) process

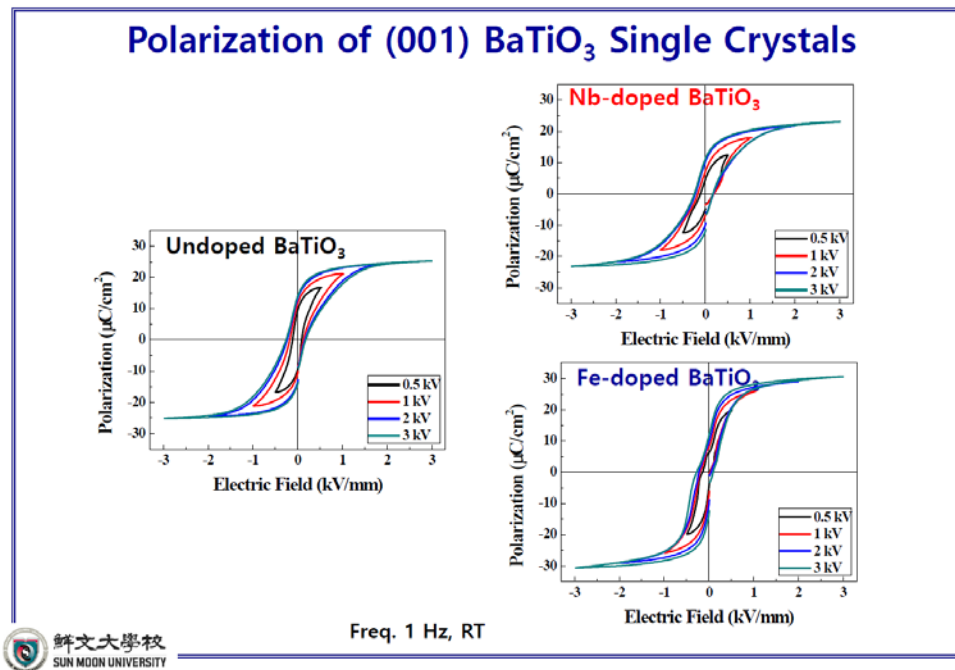


Fig. 21. Polarization vs. Electric Field of (a) undoped, (b) Fe (Acceptor)-doped and (c) Nb (Donor)-doped (001) BaTiO₃ single crystals

Bipolar Strains of (001) BaTiO₃ Single Crystals

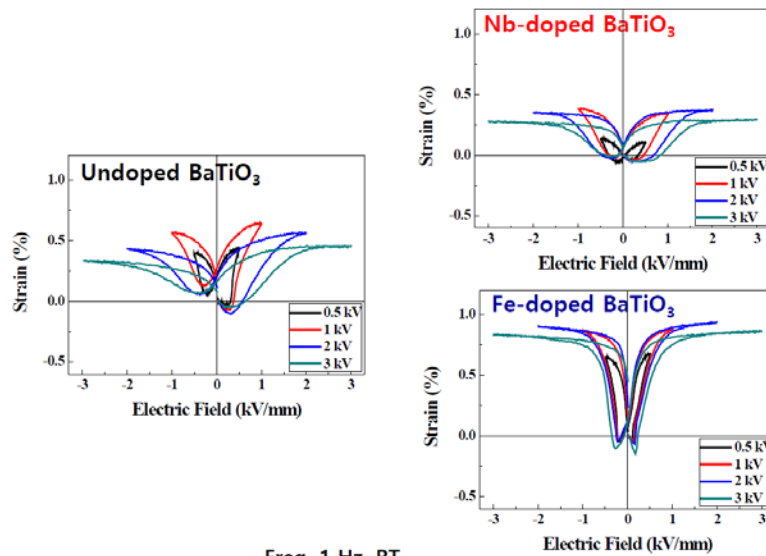


Fig. 22. Bipolar strains of (001) BaTiO₃ single crystals:
(a) undoped, (b) Nb-doped, and (c) Fe-doped

Unipolar Strains of (001) BaTiO₃ Single Crystals

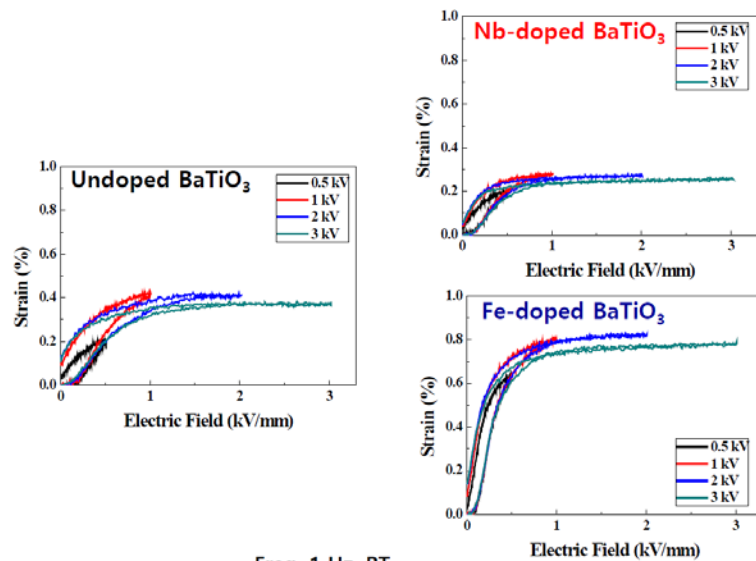


Fig. 23. Unipolar strains of (001) BaTiO₃ single crystals:
(a) undoped, (b) Nb-doped, and (c) Fe-doped

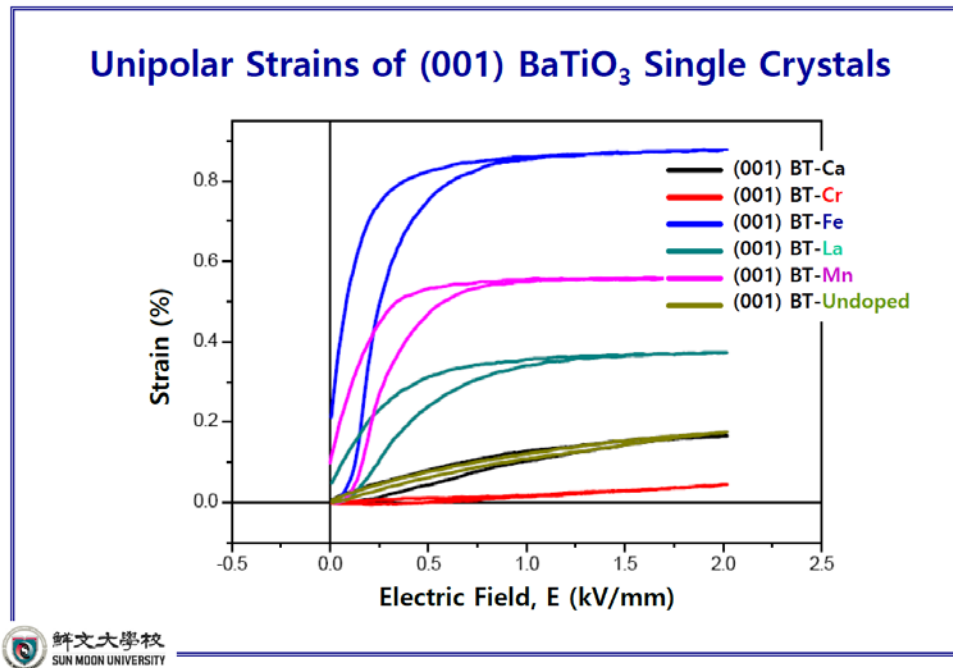


Fig. 24. Unipolar strains of (001) BaTiO₃ single crystals doped with (a) No doping, (b) Ca, (c) Cr, (d) Fe, (e) La, and (f) Mn

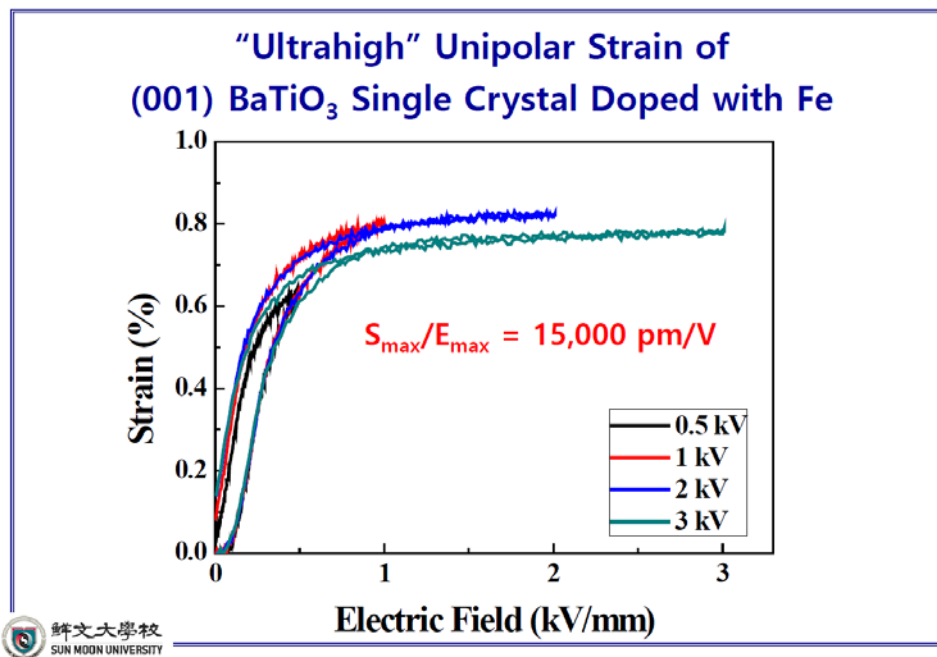


Fig. 25. “Ultrahigh” unipolar strains of (001) BaTiO₃ single crystals doped with Fe:
 $S_{\text{max}}/E_{\text{max}} = 15,000 \text{ pm/V}$

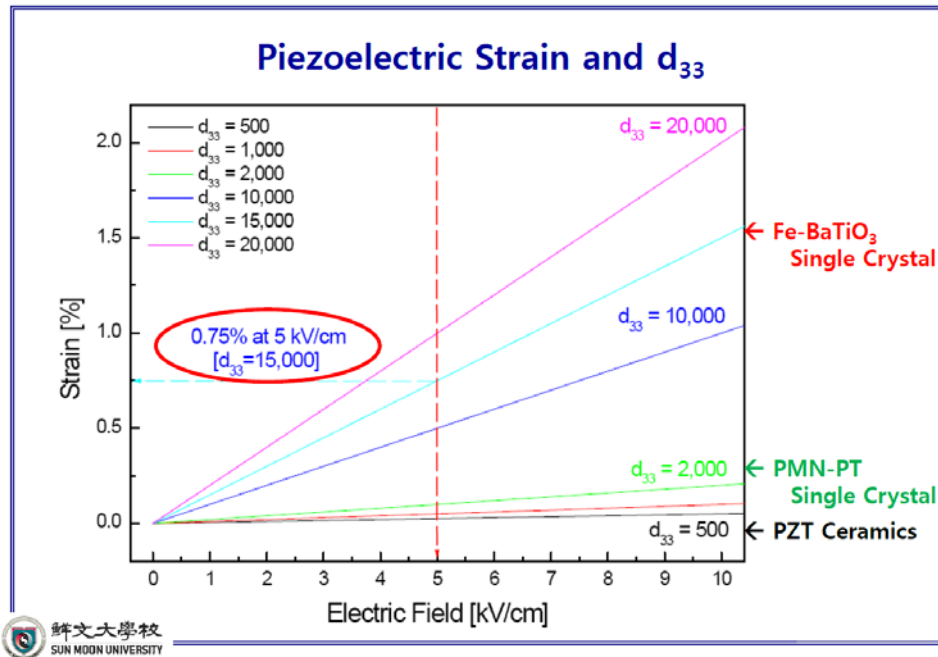


Fig. 26. “Ultrahigh” unipolar strains of (001) BaTiO₃ single crystals doped with Fe: PZT ceramics ($d \sim 500$ pC/N), PMN-PT single crystals ($d_{33} \sim 2,000$ pC/N), Fe-doped BaTiO₃ single crystals ($S_{\max}/E_{\max} = 15,000$ pm/V)

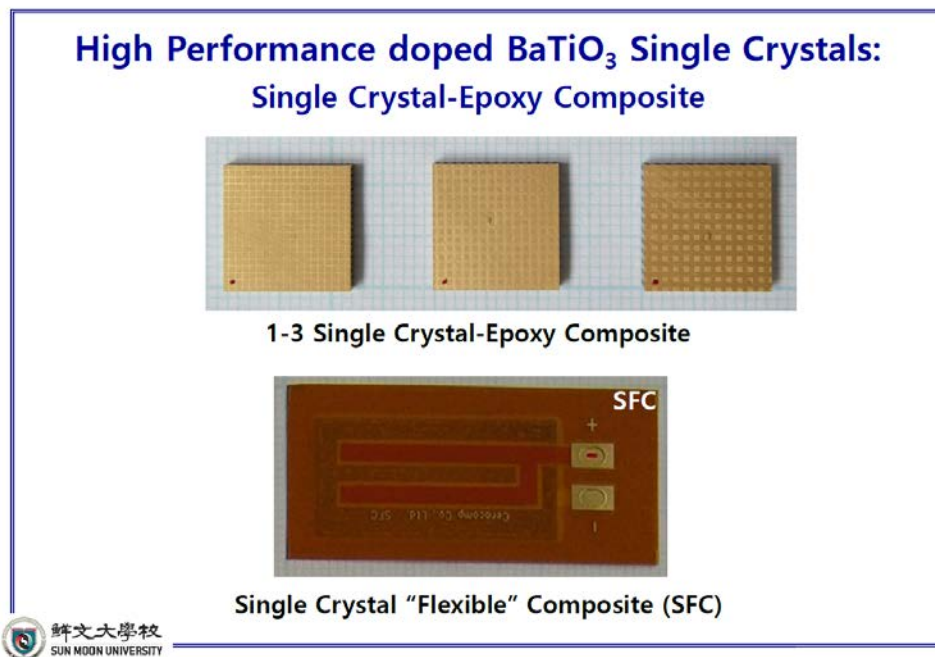


Fig. 27. Application of (001) BaTiO₃ single crystals having “ultrahigh” unipolar strains: 1-3 single crystal-epoxy composites and “flexible” SFC composites

3-2. SrTiO₃ single crystals

The single crystal growth of "*n*- and *p*-type doped" SrTiO₃ single crystals have been tried by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of SrCO₃, TiO₂, and several dopants (Ca, Ce, Co, Cr, Fe, La, Mg, Mn, Nb, and Nd), "*n*- and *p*-type doped" polycrystalline SrTiO₃ ceramics were obtained through a general sintering process. After weighing each raw material powder for "*n*- and *p*-type doped" SrTiO₃ compositions, they were mixed for 24 hours using ball-milling process, and calcined at 1,000°C following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a BaTiO₃ seed single crystal was placed on the sintered body of "*n*- and *p*-type doped" SrTiO₃, and the second heat treatment for solid-state single-crystal growth was carried out for 200 hours, as shown in Fig. 28.

The BaTiO₃ seed single crystal was placed inside SrTiO₃ ceramics and heat-treated for 200 hours. However, the growth of SrTiO₃ single crystals from the BaTiO₃ seed single crystal was very limited, as shown in Fig. 28. So the growth of SrTiO₃ single crystals was not successfully.



Fig. 28. Single crystal growth of SrTiO₃ from a BaTiO₃ single crystal seed inside SrTiO₃ ceramics

3-3. PbZrO_3 single crystals

The single crystal growth of "*n*- and *p*-type doped" PZ single crystals have been tried by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of PbO , ZrO_2 and several dopants (Ca, Ce, Co, Cr, Fe, La, Mg, Mn, Nb, and Nd), "*n*- and *p*-type doped" polycrystalline PZ ceramics were obtained through a general sintering process. After weighing each raw material powder for "*n*- and *p*-type doped" PZ compositions, they were mixed for 24 hours using ball-milling process, and calcined at 850°C following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a BaTiO_3 seed single crystal was placed on the sintered body of "*n*- and *p*-type doped" PZ, and the second heat treatment for solid-state single-crystal growth was carried out for 200 hours, as shown in Fig. 29.

The BaTiO_3 seed single crystal was placed inside PZ ceramics and heat-treated for 200 hours. However, the growth of PZ single crystals from the BaTiO_3 seed single crystal was very limited, as shown in Fig. 29. So the growth of PZ single crystals was not successfully.

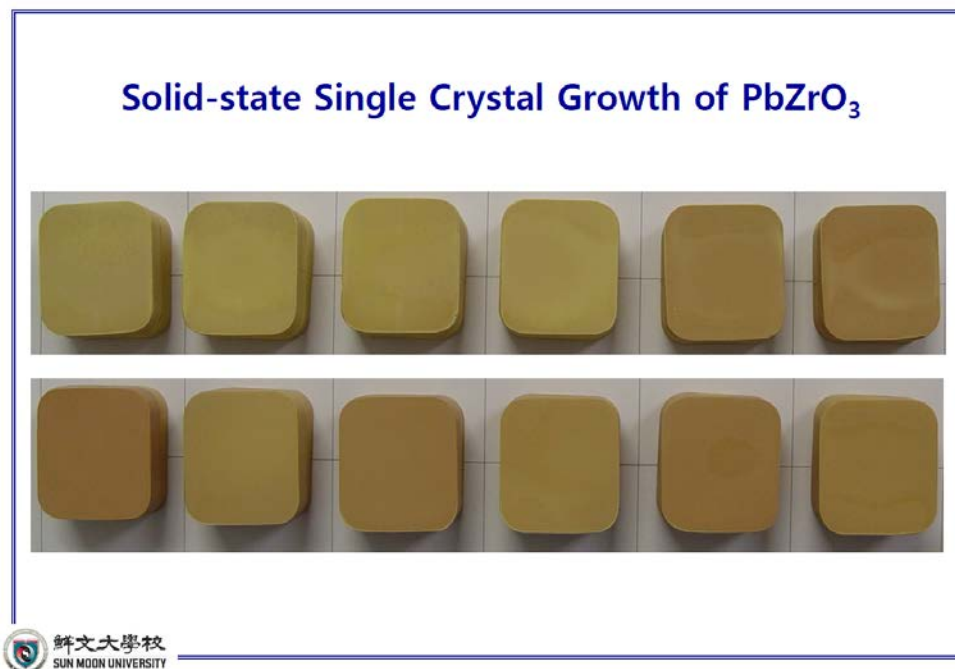


Fig. 29. Single crystal growth of PZ from a BaTiO_3 single crystal seed inside PZ ceramics

3-4. BT-BMT single crystals

The single crystal growth of "*n*- and *p*-type doped" BT-BMT single crystals have been tried by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of BaCO_3 , TiO_2 , Bi_2O_3 , MgCO_3 and several dopants (Ca, Ce, Co, Cr, Fe, La, Mg, Mn, Nb, and Nd), "*n*- and *p*-type doped" polycrystalline BT-BMT ceramics were obtained through a general sintering process. After weighing each raw material powder for "*n*- and *p*-type doped" BT-BMT compositions, they were mixed for 24 hours using ball-milling process, and calcined at 800°C following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a BaTiO_3 seed single crystal was placed on the sintered body of "*n*- and *p*-type doped" BT-BMT, and the second heat treatment for solid-state single-crystal growth was carried out for 200 hours, as shown in Fig. 30.

The BaTiO_3 seed single crystal was placed inside BT-BMT ceramics and heat-treated for 200 hours. However, the growth of BT-BMT single crystals from the BaTiO_3 seed single crystal was very limited, as shown in Fig. 30. So the growth of BT-BMT single crystals was not successfully.



Fig. 30. Single crystal growth of BT-BMT from a BaTiO_3 single crystal seed inside BT-BMT ceramics

3-5. Bi-crystals

The bi-crystals containing a twin or twist boundary have been fabricated by using (1) SSCG process and (2) diffusion-bonding process.

Figure 31 shows (a) the growth of one large single crystal from one small single crystal seed as well as (b) the growth of one large bi-crystal from one small bi-crystal seed. As shown in Fig. 31, one large bi-crystal can be easily grown from one small bi-crystal by SSCG process. However, in this process it was difficult to control a misorientation angle between two single crystals.

In order to control a misorientation angle between two single crystals more precisely, the diffusion bonding process has been developed. In this diffusion bonding process, two single crystal plates of specific crystallographic orientations are bonded under pressure at high temperature.

Figure 33 shows a process for making twist boundaries by diffusion bonding of two "same" single crystal plates of specific crystallographic orientations. In this process it was easy to control a misorientation angle between two single crystals.

Figure 34 shows a process for making twist boundaries by diffusion bonding of two "different" single crystal plates of specific crystallographic orientations. In this process it was easy to control a misorientation angle between two single crystals.

By using the diffusion bonding process developed in the program, a variety of bi-crystals are fabricated, as shown in Figs. 33 and 34.



Fig. 31. Solid-state crystal growth of (a) one single crystal seed and (b) one bi-crystal seed:
One large bi-crystal can be grown from one small bi-crystal by SSCG process.

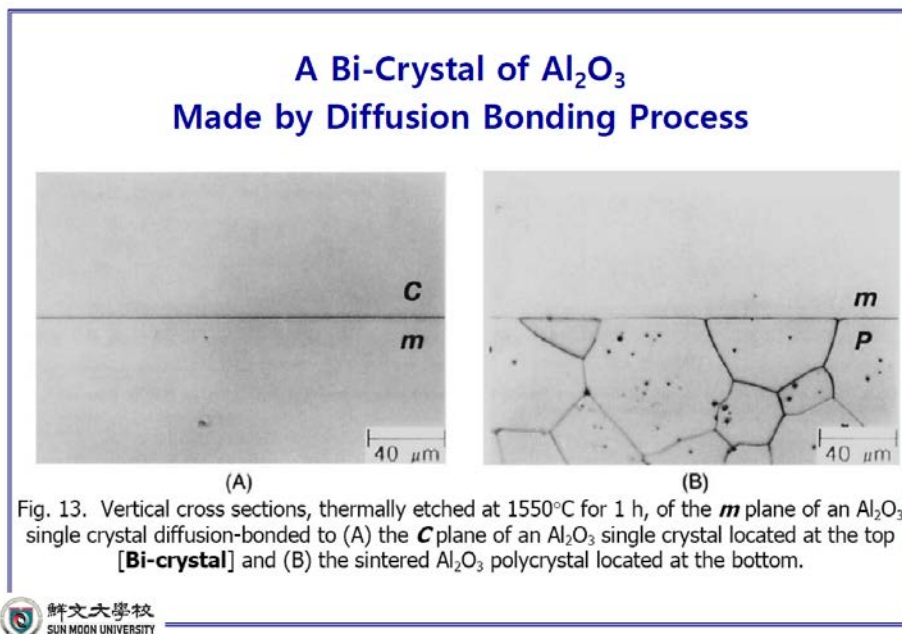


Fig. 32. Diffusion bonding process for making a bi-crystal:
Two single crystal plates are bonded under pressure at high temperature



Fig. 33. Making twist boundaries by diffusion bonding of two "same" single crystal plates with specific misorientation angles

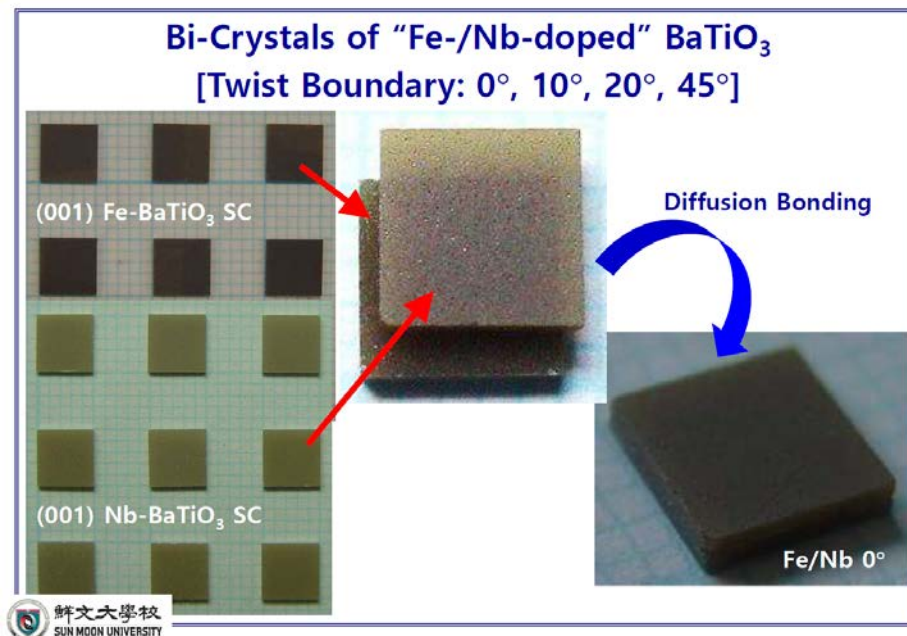


Fig. 34. Making twist boundaries by diffusion bonding of two "different" single crystal plates with specific misorientation angles

4. Conclusion

In this project the solid-state growth of “n- and p-type doped” perovskite single crystals [(1) paraelectric SrTiO₃, (2) normal ferroelectric BaTiO₃, (3) relaxor ferroelectric 0.85BaTiO₃-0.15Bi(Mg_{0.5}Ti_{0.5})O₃, and (4) antiferroelectric PbZrO₃] have been tried. Especially “n- and p-type doped” BaTiO₃ single crystals have been successfully fabricated. And their bi-crystals containing a twin or twist boundary are also fabricated using diffusion bonding process of two single crystal plates. These results demonstrate that the SSCG (solid-state single crystal growth) technique are suitable to grow a variety of “n- and p-type doped” perovskite single crystals. The principles and demonstrations are well described in the paper of Fig. 35.

The Fe-doped (001) BaTiO₃ single crystals show an ultrahigh strain of 0.8% at 1 kV/mm ($S_{\max}/E_{\max} = 15,000 \text{ pm/V}$) which is 30 times higher than PZT ceramics and 7.5 times higher than PMN-PT single crystals. Therefore the BaTiO₃ single crystals having “ultrahigh” unipolar strains will be used for actuator, sensor, and transducer applications.



Fig. 35. Solid-state conversion of single crystals: The principle and the state-of-the-art (J. Am. Ceram. Soc., 98[2], 347-360 (2015))